

HYDROGENATION OF OLEFINIC SUBSTRATES IN THE ABSENCE OF A SOLVENT

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Hydrogenation of twelve olefinic substrates in liquid phase catalysed by platinum-coated (5%) silica gel under normal conditions has been studied. The measured reaction rates and relative adsorption coefficients were correlated with polar and steric parameters by the Taft-Pavelich equation. The relative adsorption coefficients were also measured in a system of three substrates and compared with those determined by competitive hydrogenation of binary mixtures.

The structure – reactivity and structure – adsorptivity relations of organic compounds in catalytic hydrogenation have been treated in a number of papers¹⁻⁵. In most cases hydrogenation was conducted in a solvent. A solvent-free system was used, *e.g.*, by Maurel and Tellier⁶ in hydrogenation of olefins and cycloolefins. The present paper describes hydrogenation of substituted olefins in which the substituents were not only alkyls, but also aryls and groups of an ethereal or alcoholic character. Such systems extend the scales of σ^* and E_s values in a description of reactivity and adsorptivity by the Taft or Taft-Pavelich equation^{7,8}, and may reveal interactions not involved by this equation (“nonreactive” substituent – active centre of the catalyst). These interactions, if not detected, may be responsible for failure of an attempted correlation. Analogously, if a substrate fails to obey a correlation in a certain solvent only, an interfering substrate-solvent interaction must naturally be suspected. The interactions of the reacting substrates were followed by the competitive method of concurrent reactions in binary and ternary systems.

EXPERIMENTAL

Materials. Platinum-coated (5%) silica gel was prepared as previously described¹⁰, a fraction of grain size <0.063 mm being employed. The hydrogen was electrolytic; it was used without any preceding treatment. The following substrates were commercial products: 1-phenyl-2-propene (Sojuzchimexport, Moscow); *trans*-2-heptene, 2,5-dimethyl-2-hexene, 1-phenyl-2-butene (Fluka A.G., Switzerland); 1-propenyl-phenyl ether, 2-methyl-2-propen-1-ol, 2-buten-1-ol, 2-methyl-1-pentene, 4-methyl-2-pentene (Koch-Light, Coln brook, England), 1-propen-3-ol, 1-hexene (Lachema, Brno). 2,3-Dimethyl-2-butene was synthesized¹⁰ by reaction of 2-magnesiumbromopropane with acetone, followed by dehydration of the formed 2,3-dimethyl-2-butanol with 85%

phosphoric acid; rectification gave a product boiling at 75°C. All the substrates, distilled before use, were chromatographically pure.

Apparatus and methods. Hydrogenation was conducted at 20°C under an atmospheric pressure in the apparatus described¹¹, except that a miniature reactor was employed. The reactor was of glass only and was equipped with a thermostatic jacket. The reaction space had the shape of a flat-bottom flask, diameter 28 mm, height 18 mm. The neck of the flask was a tube ending in a normalized ground-glass joint, NZ 14/23. The joint was closed with a ground-glass plug, having a side tube for connexion to the measuring part of the apparatus. Through the plug was inserted a glass tube, which was drawn into a capillary reaching to above the level of the liquid in the reactor. In the capillary was a shiftable teflon tubing (diameter 0.25 mm), reaching either into the space above the liquid, to flush the reactor with hydrogen, or into the liquid, when a sample was to be withdrawn by increasing the pressure of hydrogen in the apparatus. In the upper (broad) end of the capillary tube was a silicone stopper, to tighten the passage of the teflon tubing. In the course of an experiment the tubing was closed with a steel needle. The reactor, equipped with a magnetic stirrer, was charged with 0.04 g of the catalyst and 1.5 ml of a substrate. The course of hydrogenation was followed by measuring the uptake of hydrogen with time in a gasometric burette. In concurrent (competing) reactions about 20- μ l samples were withdrawn and analysed by gas chromatography.

Analytical methods. The analyses were performed in an apparatus Chrom 2 with a flame-ionisation detector. Glass columns, packed by free pouring, were used (I: length 1.2 m, I.D. 3 mm, the bed was Reoplex 400 (5%) on Chromaton NAW, grain size 0.16–0.20 mm; II: length 4.5 m, I.D. 3 mm, bed as in I; III: parameters as with II, the bed was polyethylene glycol 6000 on Chromaton NAW, grain size 0.16–0.20 mm). The temperature was 58–153°C, depending on the nature of the analysed compounds.

RESULTS AND DISCUSSION

The kinetic measurements were performed under conditions where the reaction rate was not influenced by transport of mass⁹. The measured reaction rates recalculated for a unit quantity of the catalyst are given in Table I. They are not corrected to refer to a common partial pressure since data on the saturated vapour pressure of some substrates were not available. This fact tends to cause a slight overrating of the reactivities of higher-boiling substrates, but the differences cannot affect the results to such an extent as to distort the conclusions. The reactions were of zero order to the starting and the instantaneous concentrations of the substrates. This demonstrates that the reactions were isothermal and that the progressing conversion was not accompanied by any such change in solubility of hydrogen in the reaction system as might influence the reaction rate¹². The measured reaction rates differed from the arithmetic mean within $\pm 5\%$.

Comparison of the measured hydrogenation rates with those in solvents⁵ (substrates B, F, G, H, M) reveals that 1,4-dioxan is a solvent considerably reducing the reaction rate, and that the rate data measured in the absence of a solvent are nearest to those measured in methanol.

The relative adsorption coefficients were determined by the method of competing

reactions¹³. Pairs of substrates were so selected that the hydrogenation would be actually competitive (not selective) and the following chromatographic analysis possible (F-B, I-B, E-B, G-B, H-B, B-A, D-A, K-C, L-C, C-A, M-C). Under the assumption that no interaction of the two substrates interfered^{9,14}, recalculation gave the values of adsorption coefficients of the individual substrates related to 2,3-dimethyl-2-butene; these are also listed in Table I. Highest adsorptivity was observed with substrates with a double bond in the α -position. An only exception was 2-buten-1-ol, whose high adsorption coefficient can be ascribed to the presence of a hydroxyl group, since 1-propen-3-ol exhibited the highest adsorption coefficient of all the substrates studied. By contrast, the presence of a phenyl group markedly reduced the adsorptivity.

The effects of structure on reactivity and adsorptivity of the substrates were expressed quantitatively by the Taft⁷ and the Taft-Pavelich⁸ equations:

$$\log (r_i/r_A) = \rho_r^* \sum_1^4 \sigma_i^* + \delta_r \sum_1^4 E_s + a, \quad (1)$$

$$\log (K_i/K_A) = \rho_a^* \sum_1^4 \sigma_i^* + \delta_a \sum_1^4 E_s + b. \quad (2)$$

In addition to these fundamental forms we tested the equations without the absolute terms a and b , and also equations leaving out the steric and polar effects, invariably with and without the absolute term. The tested relations and results

TABLE I
Reaction Rates and Relative Adsorption Coefficients

Design.	Substrate	r_i	$K_{i,A}$
A	2,3-dimethyl-2-butene	7.2	1.00
B	1-phenyl-2-propene	85.3	2.53
C	2-heptene	139.2	1.10
D	2,5-dimethyl-2-hexene	21.0	1.90
E	1-phenyl-2-butene	60.4	0.07
F	1-propenyl-phenyl ether	32.9	8.45
G	2-methyl-2-propen-1-ol	38.0	2.32
H	2-buten-1-ol	44.1	19.58
I	1-propen-3-ol	31.2	83.01
K	2-methyl-1-pentene	79.7	4.27
L	4-methyl-2-pentene	35.6	1.24
M	1-hexene	100.9	59.38

of regression analysis are given in Table II. The calculation was performed with a computer Hewlett-Packard 2016 B. The values of the parameters σ^* and E_s were taken from the literature¹⁵. The isolated double bond was considered to be the reaction centre and the polar and steric constants of thus defined substituents were summarized. In the chosen model series of substrates it applies that

$$\sum_1^4 \sigma_i^* = 0.53 \sum_1^4 E_{Si} \quad (3)$$

This interdependence makes it rather impossible to distinguish strictly between the polar and the steric effects on reactivity and adsorptivity. An example of correlation of the relative reaction rates by equation (1) is shown in Fig 1; correlation of relative adsorption coefficients is exemplified in Fig. 2.

TABLE II
Results of Regression Analysis

Reaction parameters							
ρ_r	s	σ_r	s	a	s	residual spread	correlation coefficient
-0.60	0.19	0.38	0.11	0.69	0.15	0.32	0.708
-0.58	0.33	0.63	0.18	—	—	0.94	
-0.04	0.13	—	—	0.91	0.19	0.64	-0.097
0.55	0.09	—	—	—	—	2.00	
—	—	0.07	0.08	0.69	0.20	0.60	0.259
Adsorption parameters							
ρa	s	δ_2	s	b	s	residual spread	correlation coefficient
-0.11	0.77	0.56	0.46	-0.65	0.60	5.22	0.568
-0.12	0.81	0.33	0.44	—	—	5.77	
0.69	0.37	—	—	-0.28	0.53	5.08	0.466
0.50	0.15	—	—	—	—	5.22	
—	—	0.50	0.24	-0.65	0.60	5.23	0.553
—	—	0.27	0.08	—	—	5.78	

From Table II it can be seen that the reactivity and adsorptivity of a substrate is very likely to be influenced by a concerted action of the polar and the steric effects. In either case the best fitting equations were those which contained both these parameters. The correlation coefficient of the dependence of reactivity on the polar and steric parameters of the substituents exceeded the critical value for a 98% significance level. Tests with one-parameter relations were not successful. Analogously, the critical value of the correlation coefficient in testing the adsorption parameters was higher than the critical one for a 90% significance level. Even the one-parameter equation relating the relative adsorption coefficients to steric parameters of the substituents can be considered satisfactory. The greater spread of adsorption data can hardly be ascribed to the measuring error, since the accuracy in measuring the relative adsorption coefficients was no worse than that with which the rate constants were measured. The spread of data is more likely due to interfering interactions of the substituents with the active centres of the catalysts, which evidently manifest themselves more markedly as a change in adsorptivity than in reactivity. The equations with the absolute term proved more satisfactory in all cases, but its value was too low to permit a safe decision whether it was due to interactions of the substituents with the active centres of the catalysts or to the error of measurement.

In processing the data all substrates and substituents fully obeyed the correlation equations.

To obtain further information on interactions in the systems studied we hydrogenated equimolar mixtures of three olefinic substrates. The values of the relative adsorption coefficients for the three possible pairs of substrates in these mixtures were determined without taking into account every third compound. Table III

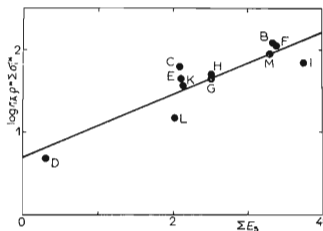


FIG. 1

Correlation of Relative Hydrogenation Rates with Polar and Steric Parameters of the Substituents

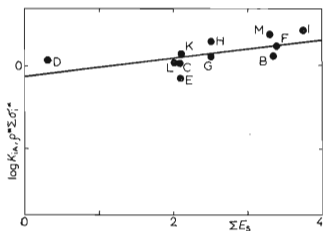


FIG. 2

Correlation of Relative Adsorption Coefficients with Polar and Steric Parameters of the Substituents

gives the relative adsorption coefficients thus obtained, along with the values determined in binary systems or obtained by recalculation from data measured in these systems (Table I). The values of $K_{x,y}^a$ were determined independently, so that they may not be related by the equation

$$K_{x,y}K_{y,z}K_{z,x} = 1. \quad (4)$$

Nevertheless, good fulfilment of the afore-said relations justifies recalculations according to equation (4). The values of $K_{x,y}^b$ also fit this equation, so that the recalculation is applicable even to mixtures of three substrates.

It has turned out that the presence of a third olefinic substrate affects the adsorption coefficients of the other two. In the first two systems (Table III) all three substrates were hydrogenated at comparable rates, so that disappearance of one substrate was not detected. In the third system hydrogenation of 2-buten-1-ol proceeded preferentially. Its disappearance from the reaction mixture manifested itself by a jump change in hydrogenation selectivity of the remaining two substrates (Fig. 3). The value of the relative adsorption coefficient $K_{B,F}$ changed from 0.44 to 0.30; the latter value was measured in competitive hydrogenation of the two compounds in a binary system.

Table III shows that the addition of an unsaturated alcohol (1-propen-3-ol, 2-methyl-2-propen-1-ol) reduces the relative adsorption coefficients of 2-buten-1-ol and 1-phenyl-2-propene; an addition of 1-propenyl phenyl ether increases this ratio. Further instances can be interpreted analogously. The experimental evidence does not allow of drawing some more general conclusions, but the method described may prove capable of affording valuable information on the interaction of substrates with solid catalysts.

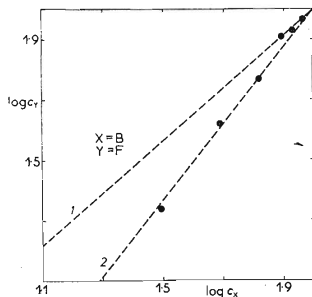


FIG. 3

Competitive Hydrogenation of 1-Phenyl-2-propene and/or 1-Propenyl-phenyl ether in Mixture with 2-Butene-1-ol

1 Course of hydrogenation in the presence of 2-butene-1-ol; 2 course of hydrogenation after 2-butene-1-ol disappeared.

TABLE III

Relative Adsorption Coefficients from Competitive Hydrogenation of Pairs and Triads of Substrates

Design.	System	X, Y	$K_{x,y}^a$	$K_{x,y}^b$	$K_{x,y}^a/K_{x,y}^b$
H	2-buten-1-ol	H, B	7.74	4.43	1.75
B	1-phenyl-2-propene	B, I	0.03	0.09	0.33
I	1-propen-3-ol	I, H	4.23	2.52	1.76
H	2-buten-1-ol	H, B	7.74	1.37	5.65
B	1-phenyl-2-propene	B, G	1.09	1.04	1.05
G	2-methyl-2-propen-1-ol	G, H	0.12	0.69	0.17
H	2-buten-1-ol	H, B	7.74	11.11	0.70
B	1-phenyl-2'-propene	B, F	0.30	0.44	0.68
F	1-propenyl-phenyl ether	F, H	0.43	0.19	2.26

^a Determined by concurrent hydrogenation of 2 substrates; ^b Determined by concurrent hydrogenation of 3 substrates.

LIST OF SYMBOLS

- a* absolute term in equation (1)
b absolute term in equation (2)
C dimensionless concentration = instantaneous concentration of compound *i* related to its initial concentration
E_S steric parameter of a substituent in the Taft-Pavelich equation
K_{i,A} adsorption coefficient of compound *i* related to that of compound A
r reaction rate (ml H₂/min g_{CAT})
r_{i,A} reaction rate of compound *i* related to that of compound A
s root-mean-square deviation
 δ parameter characterizing sensitivity of reactivity or adsorptivity to steric effect of a substituent
 q^* parameter characterizing sensitivity of reactivity or adsorptivity to polar effect of a substituent
 σ^* polar parameter of substituent in the Taft or Taft-Pavelich equation

Indices

- a* adsorption
A general designation of a substrate or 2,3-dimethyl-2-butene
i general designation of a substrate
r reaction
X, Y, Z general designation of a substrate

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